Table 1. The solubility at 25° C of calcium oxalate monohydrate in ammonium oxalate solutions and in water.

Ammonium oxalate, molarity	Ionic strength	Square of mean activity coefficient	Solubility of $CaC_2O_4 \cdot H_2O$, molarity $\times 10^6$ calculated	found
0	$1.96 \cdot 10^{-4}$	0.88	—	49.0
0.001	0.003	0.62	3.4	5.9
0.003	0.009	0.46	1.5	4.2
0.01	0.03	0.28	0.76	3.8
0.03	0.09	0.16	0.44	4.3
0.1	0.3	0.060	0.35	5.3
0.3	0.9	0.027	0.26	8.8

product was calculated to be $2.12 \cdot 10^{-9}$, using the mean activity coefficient calculated from the formula

$$-\log \gamma = 0.5\, z^2 \sqrt{\mu}/(1 + \sqrt{\mu})$$

The activity coefficients used for calculating the solubility in the oxalate solutions having an ionic strength of 0.003—0.09 were interpolated from tables published by Kielland [6]; for an ionic strength of 0.3—0.9, they have been calculated from Mc Comas and Rieman's [2] values on the solubility of calcium oxalate monohydrate in sodium chloride solutions.

The considerable differences between observed and calculated values indicate complex formation. Minimum solubility occurs at an oxalate concentration of about 0.01 *M* but the solubility differences in the concentration range 0.001—0.1 *M* ammonium oxalate are not large; 5 micromoles per litre, *i. e.* 0.2 mg Ca per litre, may be accepted as an approximate mean.

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Tetragonal Tungsten Bronzes of Degenerated Perovskite Type

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The existence of isomorphous tetragonal sodium and lithium tungsten bronzes, Me_xWO_3, of previously unknown structural type was reported in a recent paper from this Institute [1]. This note will present an account of the determination of the crystal structure of these compounds.

The investigation was based on powder and single crystal photographs of the sodium compound, the preparation examined having the composition $Na_{0.10}WO_3$. The radiation used was Cu-*K*. The lattice constants of the tetragonal unit cell, as obtained from the powder photographs are (referred to the wave-length of Cu-*Ka* radiation equal to 1.5418 Å):

$$a = 5.248 \text{ Å}, \quad c = 3.895 \text{ Å}, \quad V = 107.3 \text{ Å}^3$$

The observed density of 7.25 corresponds to a cell content of 2 formula units of $Na_{0.10}WO_3$.

The Laue symmetry was found from Weissenberg photographs to be *4/mmm*. The only systematic absences are *hk*0 reflections with $h + k$ odd, which unequivocally suggests *P4/nmm* as the most probable space-group.

A striking feature of the diffraction pattern is the decisive significance of the *l* index for the intensities of the reflections. In rough outline the following regularities could be observed:

for reflections *hkl* ($h + k$ even): *hk*0 (strong), *hk*1 (strong), *hk*2 (medium), *hk*3 (weak), *hk*4 (not visible), *hk*5 (weak, only β reflections observed);

for reflections *hkl* ($h + k$ odd): *hk*0 (absent), *hk*1 (medium), *hk*2 (medium), *hk*3 (medium), *hk*4 (medium).

Table 1. Observed and calculated intensities in Weissenberg photographs of $Na_{0.10}WO_3$. Rotation axis [110]. Cu-K radiation.

Zero layer line:

110^{vst}_{79} 220^{vst}_{23} 330^{m}_{10} 440^{m}_{8} $550(\beta)^{w}_{1.2}$

001^{vst}_{76} 111^{vst}_{38} 221^{st}_{15} 331^{m}_{7} 441^{m}_{7} $551(\beta)^{w}_{2}$

002^{st}_{12} 112^{m}_{10} 222^{m}_{5} 332^{m}_{3} 442^{m}_{5}

$003^{w}_{1.2}$ $113^{w}_{1.0}$ $223^{w}_{.8}$ $333^{w}_{1.0}$ $443(\beta)^{-}_{.1}$

$004^{-}_{.02}$ $114^{-}_{.02}$ $224^{-}_{.02}$ $334(\beta)^{-}_{.005}$

$005(\beta)^{vw}_{.2}$ $115(\beta)^{vw}_{.2}$ $225(\beta)^{vw}_{.4}$

First layer line:

010^{-}_{0} 120^{-}_{0} 230^{-}_{0} 340^{-}_{0} 450^{-}_{0}

011^{st}_{11} 121^{m}_{4} $231^{w}_{1.9}$ $341^{w}_{1.1}$ 451^{m}_{3}

012^{st}_{12} 122^{m}_{7} 232^{m}_{4} 342^{m}_{4}

013^{m}_{8} 123^{m}_{7} 233^{m}_{6} 343^{st}_{12}

014^{m}_{7} 124^{m}_{8} 234^{st}_{15}

Second layer line:

020^{vst}_{60} 130^{vst}_{20} 240^{m}_{8} 350^{m}_{9}

021^{vst}_{33} 131^{st}_{14} 241^{m}_{6} 351^{m}_{8}

022^{m}_{8} 132^{m}_{5} 242^{w}_{3} 352^{m}_{7}

$023^{-}_{1.1}$ $133^{-}_{.8}$ $243^{-}_{1.2}$

$024^{-}_{.02}$ $134^{-}_{.02}$

Third layer line:

030^{-}_{0} 140^{-}_{0} 250^{-}_{0}

031^{m}_{3} $141^{w}_{1.5}$ $251^{w}_{1.3}$

032^{m}_{6} 142^{m}_{4} 252^{m}_{5}

033^{m}_{7} 143^{m}_{8} 253^{st}_{23}

034^{m}_{11}

Fourth layer line:

040^{st}_{15} 150^{m}_{8} 260^{st}_{13}

041^{m}_{11} 151^{m}_{7} 261^{st}_{13}

042^{m}_{4} 152^{m}_{4}

$043^{vw}_{1.0}$ 153^{w}_{2}

$044^{-}_{.1}$

vst = very strong, st = strong, m = medium, w = weak, vw = very weak

A close examination furthermore revealed that the structure amplitudes $|F(hkl)|$ of the reflections of each of these two series are, within the error of estimation, independent of the values of h and k, but varying with l only. These regularities can only be accounted for if the two tungsten atoms of the unit cell occupy a twofold point position $2(c): 0\,\frac{1}{2}\bar{z}$, $\frac{1}{2}0z$, with $\bar{z}$ equal to 0.065 ± 0.01 or 0.435 ± 0.01. The latter value of the parameter will be arbitrarily adopted for the following discussion. Table 1 gives a comparison between the observed intensities and those calculated on the basis of this arrangement of the tungsten atoms.

It is not possible to find the positions of the oxygen and sodium atoms from

the X-ray data as the scattering power of these atoms is too low in comparison with that of the tungsten atoms. The arrangement of the latter, however, is very similar to that derived by Hägg [2] for the cubic sodium tungsten bronze of perovskite type. This fact suggests that the two structures are closely related, and leads to the following atomic configuration of the tetragonal bronze, which corresponds throughout to plausible interatomic distances:

Cell content: $2\ Na_xWO_3$
Space-group: $D_{4h}^7 - P4/nmm$
2 W in 2(*c*): $0\frac{1}{2}z$, $\frac{1}{2}0\bar{z}$ $z = 0.435$
$2x$Na in 2(*a*): 000, $\frac{1}{2}\frac{1}{2}0$
2 O in 2(*c*): $0\frac{1}{2}z$, $\frac{1}{2}0\bar{z}$ $z \approx 0.935$
4 O in 4(*e*): $\frac{1}{4}\frac{1}{4}\frac{1}{2}$, $\frac{3}{4}\frac{3}{4}\frac{1}{2}$, $\frac{1}{4}\frac{3}{4}\frac{1}{2}$, $\frac{3}{4}\frac{1}{4}\frac{1}{2}$

The structure may be described as built up of deformed WO_6 octahedra, joined by sharing corners. The alkali metal atoms are statistically distributed and occupy approximately 10 per cent of the major interstices of the lattice. (It must be emphasized that this scheme presupposes the unit cell dimensions and symmetry of the actual structure to be identical with those of the tungsten lattice.)

The tungsten atoms form puckered networks extending parallel to the *ab* plane, by being a little displaced alternately + 0.25Å and − 0.25 Å in the direction of the *c* axis. In this respect which constitutes the difference from a lattice of perovskite type, the structure is reminiscent of the tungsten trioxide structure of deformed ReO_3-type, the metal atoms of which show similar displacements parallel to two of the axes of the cubic substructure cell (± 0.23 Å and ± 0.24 Å respectively)[3]. It is noteworthy that another tetragonal sodium tungsten bronze, $Na_xWO_3 (x \approx 0.3)$, of complicated structure also contains puckered networks of tungsten atoms [4].

These structural relationships evidently demonstrate the character of the bronzes of degenerated perovskite type to be a distinct intermediate state in the transitions with decreasing alkali metal content from the cubic sodium [2] and lithium [5] bronzes of perovskite type to tungsten trioxide.

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Estimation of Xylocaine * by Nitration

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Comprehensive experiments have shown that Xylocaine (α-diethylamino-2,6-acetoxylidide) can be nitrated in a simple manner with analytical reproducibility. However the nitration conditions must be rigidly controlled since the course of the reaction is easily affected by variations in the reagent and the temperature employed. Nitration at 80° C with one part of conc. nitric acid and five parts of acetic acid seems to be most suitable. Hydrogenation of the nitration product is subject to similar limitations. The method would appear to be specially suitable for estimation of Xylocaine in small amounts, in dilute solutions and possibly also in biological material. The procedure and applicability of the method are being further investigated at present.

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